UNIVERSITY OF PENNSYLVANIA

THE ACTIVITY COEFFICIENTS OF ALKALI HYDROXIDES IN ALKALI CHLORIDE SOLUTIONS

JOHN McARTHUR HARRIS, JR.

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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INTRODUCTION

When two uniunivalent electrolytes are mixed in aqueous solution and their concentrations are varied in such a manner that the total molality of the mixture remains constant, the relation between γ, the activity coefficient of one of the electrolytes and C, the concentration of the same electrolyte is given by the equation

$$\log \gamma = \alpha C + \text{constant}$$

where α is a constant. When C equals O, the term α C drops out and the second constant of the equation becomes equal to log γ_0 where γ_0 is the activity coefficient at zero concentration. The equation may, therefore, be written

$$\log \gamma = \alpha C + \log \gamma_0$$

An extensive study of this law has been made by Harned,[1] Brönsted,[2] Harned and Brumbaugh,[3] and Harned and Åkerlöf.[4] Guntelberg[5] has made measurements of extreme accuracy in this connection.

These investigations have shown that the law is valid for the activity coefficients of hydrochloric acid in solutions of uniunivalent chlorides, up to a total concentration of six molal.

The object of this investigation was to submit the law of the linear variation of the log γ to a more severe test.

The thermodynamic properties of the alkaline hydroxides differ from those of the corresponding chlorides. For example, sodium chloride has a higher activity coefficient than potassium chloride while the opposite is true of the corresponding hydroxides. This fact indicates that sodium hydroxide is less normal than the other simple electrolytes. Therefore, if any exceptions to the law are to be found, an investigation of sodium hydroxide-sodium chloride mixtures should bring one to light.

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[1] Harned, J. A. C. S., 42, 1808 (1920).
[2] Brönsted, J. A. C. S., 44, 938 (1922).
[3] Harned and Brumbaugh, J. A. C. S., 44, 2729 (1922).
[4] Harned and Åkerlöf, Physik, Z. 27, 411 (1926).
Guntelberg, Z. physik. Chem., 123, 199 (1926).

Sodium hydroxide-sodium chloride and potassium hydroxide-potassium chloride mixtures have been already investigated at total concentrations up to three molal. From the few results available for testing the law, indications were obtained that there was but little departure from linearity. Since these previous studies did not constitute an exhaustive test, the following measurements were made.

Materials

A high grade of chemicals was used.

Potassium Hydroxide:

A concentrated solution of potassium hydroxide of about 30 per cent strength was prepared. The required weight of the solid caustic was weighed out and dissolved in ten litres of freshly distilled water. After the solution had cooled, a saturated solution of barium hydroxide was added drop by drop, the solution being thoroughly agitated and allowed to settle for fifteen minutes after the addition of each drop. The potassium hydroxide seemed to be remarkably free from carbonate as there was no further precipitation after the addition of four or five drops. The solution was finally filtered through asbestos, directly into a ten-litre bottle which was connected to a burette by means of a syphon and protected with soda-lime tubes.

A portion of this concentrated solution was drawn off into a twenty-litre bottle containing the proper amount of freshly distilled water to make a one-tenth molal solution. This second bottle was equipped with a syphon and soda-lime tubes and this solution was used as the "reference" solution.

Sodium Hydroxide:

A carbonate free solution of sodium hydroxide was prepared by making up a saturated solution of the hydroxide, in which the carbonate is insoluble, and filtering this solution through asbestos into a ten-litre bottle which contained sufficient freshly distilled water to produce ten litres of 25 per cent solution. This bottle was equipped with syphon, burette, and soda-lime tubes.

A dilute solution of sodium hydroxide was prepared from the concentrated solution in the manner described for the dilute solution of potassium hydroxide, and was used as the "reference" solution in the sodium hydroxide-sodium chloride series of measurements.

Fresh solutions were prepared for each of the series of measurements on the sodium hydroxide-sodium chloride mixtures.

Hydrochloric Acid of known strength was prepared from the "constant boiling" acid by diluting it until it was about normal and finally determining the exact strength by weighing the silver chloride precipitated from a given volume of the acid.

The (weight) molality of all the hydroxide solutions was determined by titration of weighed samples of the hydroxide with this standard acid.

Sodium Chloride and *Potassium Chloride* were dried at 118 degrees for at least twenty-four hours and were then ready for use.

Amalgams: Sodium and Potassium amalgams were prepared and kept as described by Harned.[6]

Apparatus and Method of Measurement

The apparatus used was essentially the same as that of Harned and Åkerlöf:[7] It is illustrated in Figure I.

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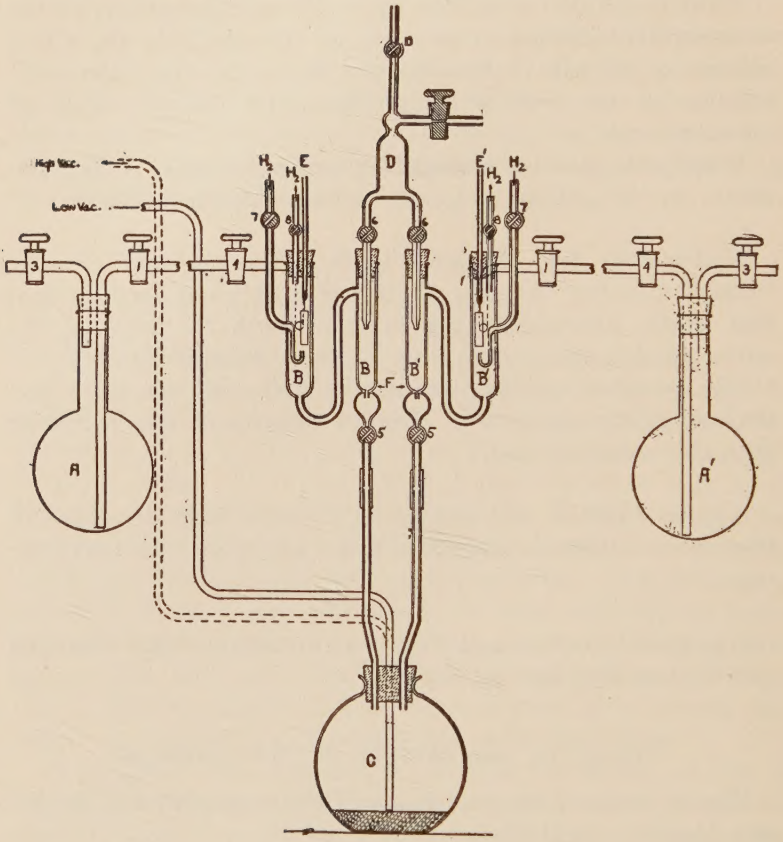
[6] Harned, J. A. C. S., 47, 676 (1925).
[7] Harned and Åkerlöf, Physik., 2, 27, 411 (1926).



Three series of measurements were made:

a. The E. M. F. of the cell

$$H_2 \mid KOH\ (m)\ KCl\ (m_1) \mid K_x\ Hg \mid KOH\ (0.108) \mid H_2$$

was measured. m, the molality of the potassium hydroxide in the left-hand side of the cell, varied from .5 M to 3.5 M. and m, the molality of the potassium chloride in the left-hand side of the cell varied from 3 m to zero. The changes in concentration were made by increments .5 M and the relation m

plus m_r equals 3.5 was maintained throughout the series. The right-hand side of the cell contained a 0.108M potassium hydroxide solution which was the "reference" solution for the series.

b. The E. M. F. of the cell

H_2 | NaOH (m) NaCl (m_r) | Na_xHg | NaOH (0.108) | H_2

was measured, m was varied from .5M to 5M and m_r, from 4.5 M to zero. The relation, m plus m_r equals 5, was maintained and the "reference" solution was 0.108 M sodium hydroxide.

c. The E. M. F. of the cell,

H_2 | NaOH (m) NaCl (m_r) | Na_x Hg | NaOH (0.106) | H_2

was measured, m was varied from 3. to .5 M and m_r, from zero to 2.5 M. The relation m plus m_r equals 3 was maintained and the "reference" solution was 0.106 M sodium hydroxide.

The method of measurement was as follows:

The flask A, after a thorough washing with distilled water, followed by alcohol, was dried with a current of air, evacuated and weighed. The flask was then weighed without its stopper and delivery tubes and the required amount of salt weighed out in the open flask. The stopper was then replaced and the flask again evacuated and weighed. Next the required amount of carbon dioxide free water, plus about 6 c. c., was run into the flask and after a third evacuation the flask was again weighed. Air was then let into the flask and the required amount of the concentrated hydroxide solution run in. The flask was again evacuated and weighed and, after letting in a few bubbles of air to minimize "bumping", the contents of the flask were boiled until about 5 grams of water had been lost.

After a final weighing and cooling, the space above the solution was filled with nitrogen and the flask connected to the cell as shown in Figure I.

The weighings made during the preparation of a solution in flask A were:

Weight of flask—	194.34	air pumped out of flask before each weighing
Weight of KCl + "	231.78	
Weight of H_2O + " + "	487.50	
Weight of KOH + " + " + "	607.30	
" " " " " + " after boiling—	598.10	

From these readings the molal concentrations of the salt and the hydroxide can be readily calculated.

Flask A was washed, dried, evacuated and weighed; then filled with about 400 c. c. of the "reference" solution, evacuated and weighed again. After a few bubbles of air had been admitted the contents of the flask were boiled until 4 or 5 grams of water had been lost when the flask was weighed the third time. Finally, it was allowed to cool, the space above the solution filled with nitrogen, and the flask then connected to the cell as shown in Figure I.

Before each measurement the hydrogen electrodes, E and E′, were given a fresh coating of platinum black and placed in the electrode compartments as shown.

The two tubes which later hold the amalgam dropper D were closed with rubber stoppers, stopcocks 5.5 were opened, all other stopcocks closed, and the cell evacuated through the high vacuum line which led to an oil pump and manometer. After a good vacuum had been obtained, stopcocks 5.5 were closed and by opening stopcocks 1,1 and 4,4 cell B was filled with the solution from A and B′ with the solution from A′. Stopcocks 1,1 and 4,4 were then closed and 5,5 opened whereby the cell was drained into the receiver C. When a good vacuum had again been obtained stopcocks 5,5 were closed and the cell filled with solution as before. This process was repeated until by three fillings and drainings the cells had been thoroughly washed. The fourth filling was allowed to remain in the cell.

The amalgam dropper after careful cleaning and drying was filled with amalgam, after first sucking pure mercury up into the limbs so as to fill them to a point just above stopcocks 6,6. The filled dropper was removed from the vacuum line, the portion of the tube above stopcock 10 filled with water, and the dropper then placed in the cell in the position shown. Great care was

taken to seat the dropper as quickly as possible after the removal of the rubber stoppers, used during the filling of the cell, in order to prevent as far as possible the absorption of oxygen and carbon dioxide from the air. As the limbs of the dropper always displace a small amount of the solution from the cell causing it to overflow into the thermostat, the dropper can be seated so as to leave no air bubbles in the cell.

Before finally pressing the dropper into position, stopcocks 8,8 are opened so as to avoid compression in the cell. Stopcocks 7,7 are opened to permit the passage of a slow stream of hydrogen through the electrode compartments. After leaving the cell through stopcocks 8,8, the hydrogen is led up to a hydrogen trap (not shown in Figure I) so that if for any reason the current of gas were interrupted the electrode compartments would remain full of hydrogen. After the hydrogen had passed through the cell for about ten minutes, by cautiously opening stopcocks 5,5 the level of the solutions in the electrode compartments was adjusted so that the platinum electrodes were one-half immersed.

After a period of from two and a half to three hours, during which the hydrogen electrodes come to equilibrium, the reading is taken as follows:

The electrodes, E,E′ are connected to the potentiometer and a good vacuum obtained in C. Stopcock 10 is opened whereupon the water above it is sucked into the dropper and protects the amalgam from contact with the air. 6,6. are opened wide and a fine unbroken thread of the amalgam passes into B and B′ collecting in puddles at F. 5,5 are adjusted so that the size of these puddles remains constant, the excess amalgam draining into C. Thirty seconds after the opening of 6,6, the time required to drain the pure mercury out of the limbs of the dropper, the first reading is taken on the potentiometer. The dropper drains in from five to ten minutes during which period twenty to thirty readings of the E. M. F. of the cell can be made, the mean of which is taken as the final value.

After each measurement flasks A and A′ are removed at once, washed out with water and alcohol, and dried. The amalgam dropper is removed and washed out by sucking water through it with a water aspirator. The cell itself is washed by sucking

distilled water through 4,4 and also, after removal of the platinum electrodes, by filling the cell several times with distilled water and draining into C.

The accumulation in C is finally sucked off into another bottle, outside of the thermostat, through the low vacuum line. Sufficient mercury must always be kept in C to prevent it from having a tendency to float and break the apparatus.

Care must be taken not to leave the strong caustic solutions in the apparatus overnight as the stopcocks would "freeze".

It is obvious that, by boiling the solutions to expel the dissolved oxygen, the concentrations of the solutes are changed slightly. The E. M. F. of the concentrations measured may be corrected, without appreciable error to the E. M. F. of the desired concentrations by the formula,

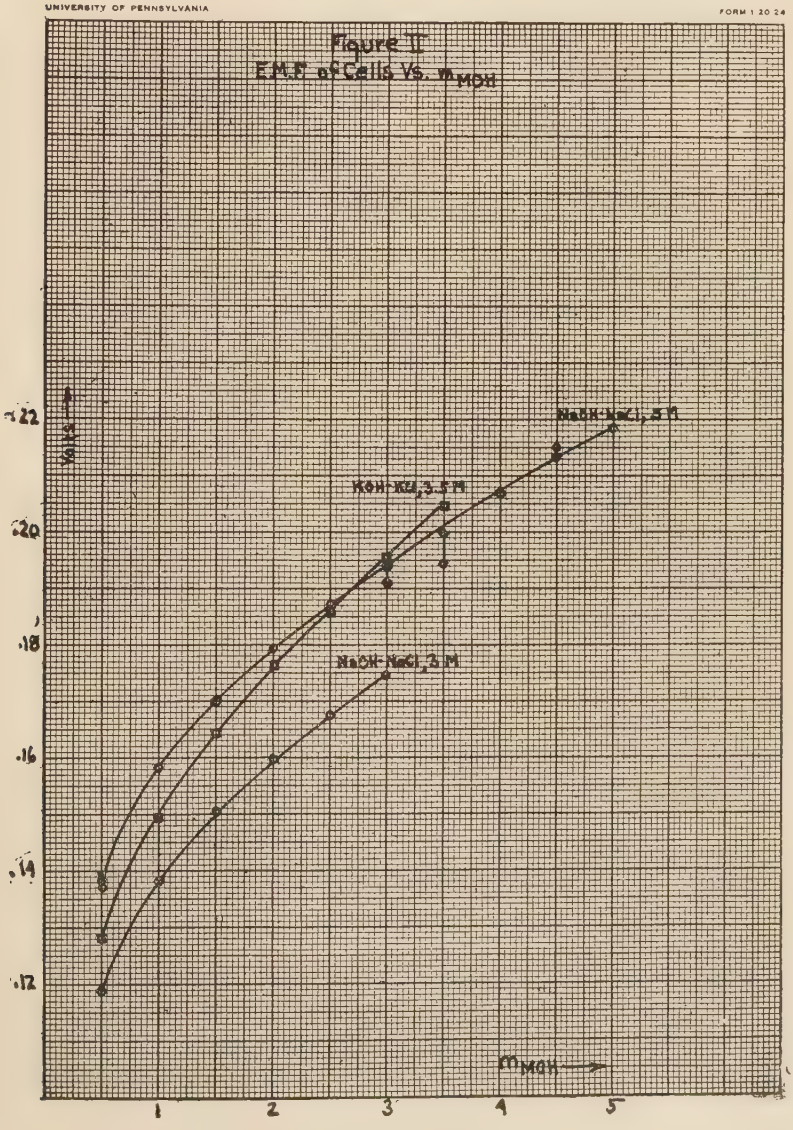
$$\Delta E = -\left[.05915 \log \frac{m_{Na\ (\text{after boiling})}}{m_{Na\ (\text{desired}} + .05915 \log \frac{m_{OH\ (\text{after boiling})}}{m_{OH\ (\text{desired})}}\right] + .1183 \log \frac{m_{NaOH\ (\text{after boiling})}}{m_{NaOH\ (\text{desired})}}$$

where the term in square brackets refers to the concentrations in the sodium hydroxide – sodium chloride mixtures, and the last term to the concentrations of the sodium hydroxide in the reference solution.

The formula employed for the correction of the E. M. F. in the potassium hydroxide-potassium chloride mixtures is identical to the above.

The corrected values for the E. M. F.'s of the different series are given in tables I, II and III and these results are plotted in Figure II. At least two measurements were made for each point on the curves. In cases where the two values agreed to within .2 millivolt, the mean was plotted, otherwise the value falling on the E. M. F. curve was taken as the correct one. In one case three determinations of one point are plotted. The

first two differed by more than a millivolt but as the third checked the mean of the first two, it was taken as the correct value.



Calculation of Activity Coefficients

Series A. The activity coefficients of potassium hydroxide may be calculated from the E. M. F. of the cell.

H_2 | KOH(m) KCl(m_1) | Kx Hg | KOH (0.108) | H_2

by means of the formula:

$$[\text{at } 25°C]\ E = -.05915 \log \frac{a_{K(S)} \cdot a_{OH(S)}}{a_{K(.108M)}\ a_{OH(.108M)}} \cdot \frac{a_{H_2O\ (.108M)}}{a_{H_2O(S)}}$$

where: $^aK(S)$ is the activity of the potassium in the KOH-KCl mixture.

$^aOH(S)$ the activity of the hydroxyl group in the mixture.

^aK (0.108M) the activity of the potassium in the 0.108M KOH reference solution.

^aOH (.108m) the activity of the hydroxyl group in the reference solution.

^aH_2O (.108m) the activity of the water in the .108M NaOH reference solution.

^aH_2O the activity of the water in the KOH-KCl mixture.

Since the activity is related to m the stoichiometric molality and the activity coefficient by the equation equals
We may write:

$$[\text{at } 25°C]\ \text{E. M. F.} = .05915 \log \frac{\gamma_{K(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}} \cdot \frac{a_{H_2O\ (0.108)}}{\gamma_{K(a.108)}\ \gamma_{OH(a108)}} \cdot \frac{m_{K(S)}\ m_{OH(S)}}{(0.108)_2}$$

assuming that the term $\frac{a_{H_2O\ (0.108)}}{\gamma_{K(0.108)}\ \gamma_{OH(0.108)}}$ is constant and equal to unity.

$$E = .05915 \log \frac{\gamma_{K(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}} \times \mid x \frac{[m_{KCl(S)} + m_{KOH(S)}]\ m_{KOH(S)}}{(0.108)_2}$$

$$E = .1183 \log \sqrt{\frac{\gamma_{K(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}} \sqrt{\frac{[m_{KCl(S)} + m_{KOH(S)}]\ m_{KOH(S)}}{(0.108)_2}}$$

since $[m_{KCl(S)} + m_{KOH(S)}]$ is constant and equal to 3.5

$$E = .1183 \log \sqrt{\frac{\gamma_{K(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}} \frac{\sqrt{3.5 \times m_{KOH(S)}}}{0.108}$$

$$\frac{E}{.1183} = \log \sqrt{\frac{\gamma_{K(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}} + \log \frac{\sqrt{3.5 \times m_{KOH(S)}}}{0.108}$$

$$\log \sqrt{\frac{\gamma_{K(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}} = \frac{E}{.1183} - \log. \frac{\sqrt{3.5 \times m_{KOH(S)}}}{0.108}$$

The activity coefficient of potassium hydroxide is defined as $\sqrt{\gamma OH\ \gamma K}$. Therefore the first term in the above equation is the desired coefficient divided by the square root of the activity of the water present. As the activity of the water is very small, values of the expression $\sqrt{\frac{\gamma_{K(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}}$ may be taken as values of the activity coefficient of the potassium hydroxide.

Since we have assumed that the term

$$\frac{a_{H_2O}\ (0.108)}{\gamma_{K(0.108)}\ \gamma_{OH(0.108)}}$$

is constant and equal to unity the values of γ_{KOH} as calculated above will be referred to the activity of .108 M KOH as unity. The actual value of $\gamma_{KOH(0.108M)}$ is .776; therefore, if the above values are all multiplied by .776 the products will be the actual activity coefficients.

Series B. The activity coefficients of sodium hydroxide in sodium chloride solutions may be calculated from the values of the E. M. F. of the cell.

$H_2 \mid NaOH(m)\ NaCl(m_1) \mid Na_xHg \mid NaOH(0.108) \mid H_2$

by the formula:

$$[\text{at } 25°C]\ E = .05915 \log \frac{a_{Na(S)} a_{OH(S)}}{a_{Na(a108)}\ a_{OH(0.108)}} \cdot \frac{a_{H_2O(0.108)}}{a_{H_2O(S)}}$$

[The system of symbols used is the same as for Series A.]

$$\text{or } E = .05915 \log \frac{\frac{\gamma_{Na(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}}{\frac{m_{Na(S)}\ m_{OH(S)}}{(0.108)_2}} \cdot \frac{a_{H_2O(0.108)}}{\gamma_{Na(0.108)}\ \gamma_{OH(a108)}}$$

assuming that the term $\frac{a_{H_2O(0.108)}}{\gamma_{Na(0.108)}\ \gamma_{OH(1.108)}}$ is constant and equal to unity and as $[m_{NaOH(S)} + m_{NaCl(S)}] = 5$

$$\log \sqrt{\frac{\gamma_{Na(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}} = \frac{E}{.1183} - \log \frac{\sqrt{5 \times m_{NaOH(S)}}}{0.108}$$

The expression $\sqrt{\frac{\gamma_{Na(S)}\ \gamma_{O(HS)}}{a_{H_2O(S)}}}$ gives values of the activity coefficient of sodium hydroxide (γNaOH) referred to the activity coefficient of 0.108 M sodium hydroxide as unity. Actually γNaOH(0.108M) = .757, therefore, if the values as derived above are multiplied by .757 the products will be the true activity coefficients.

Series C. From E. M. F. measurements of the cell

$$H_2 \mid NaOH(m)\ NaCl(m_1) \mid Na \times Hg \mid NaOH(0.106) \mid H_2$$

the activity coefficients of the sodium hydroxide in the chloride mixture are calculated by the equation

$$[\text{at } 25°C]\ E = .05915 \log \frac{a_{Ha(S)}\ \ a_{OH(S)}}{a_{Na(0.106)}\ \ a_{OH(0.106)}} \cdot \frac{a_{H_2O(0.106)}}{a_{H_2O(S}}$$

(System of symbols as in Series A and B.)

In this case $[^mNaOH(S) + {}^mNaCl(S)] = 3$ and the reference solution was 0.106 molal sodium hydroxide.

The final equation is $\log \sqrt{\frac{\gamma_{Na(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}} = \frac{E}{.1183}$

$$\log \frac{\sqrt{3 \times m_{NaOH(S)}}}{0.106}$$

The term $\sqrt{\frac{\gamma_{Na(S)}\ \gamma_{OH(S)}}{a_{H_2O(S)}}}$ gives values of γNaOH referred to γNaOH at 0.106 M as unity. The correct value of γ NaOH(0.106M) equals .758; therefore, the values as obtained above must be multiplied by .758 to get the correct values.

Figure III gives values of log γ_{KOH} plotted against the concentration of the potassium hydroxide.

Figure IV gives values of log γ_{NaOH} plotted against the concentration of the sodium hydroxide. The two curves represent the series of 5 Molal total molality and 3 M total molality.

Tables I, II and III give the corrected values of the E. M. F. and the activity coefficients calculated from them.

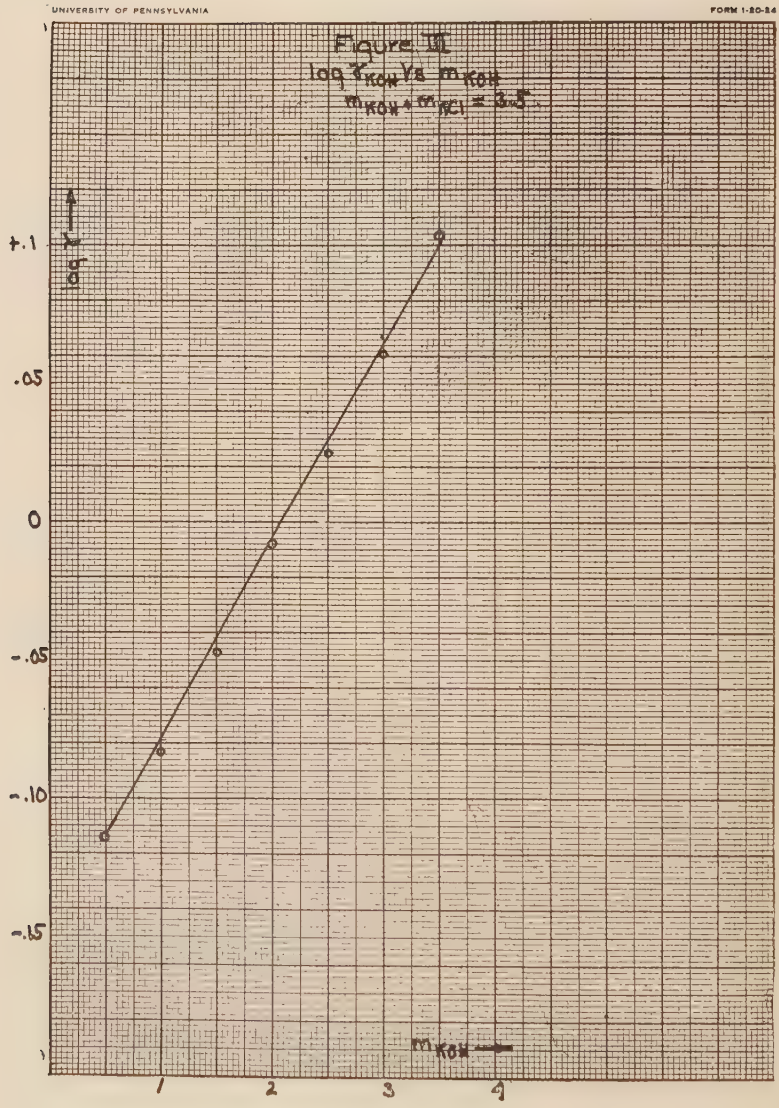

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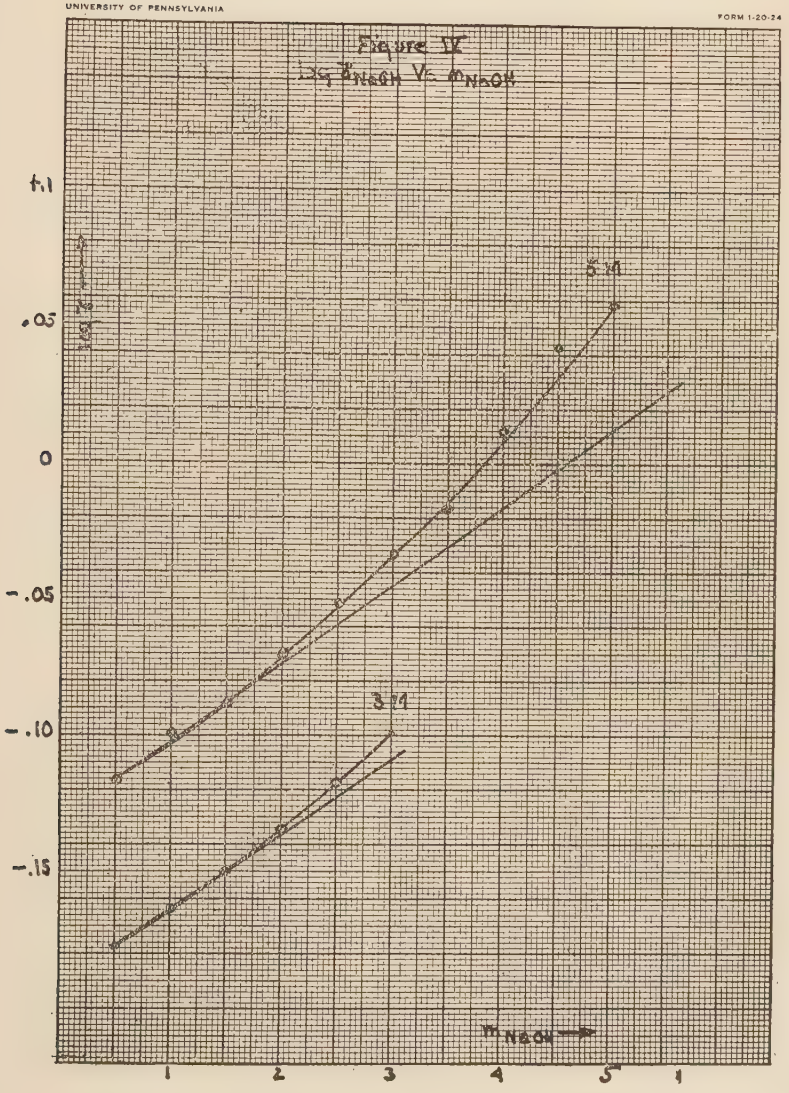
Figure III
log γ KOH Vs m KOH
m KOH + m KCl = 3.5
log γ KOH
+.1
.05
0
-.05
-.10
-.15
m KOH
1
2
3
4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FORM 1-20-24
Figure IV
.1
.05
0
-.05
-.10
-.15
5 M
3 M
1
2
3
4
5
1

TABLE I

Series A

Activity Coefficient Data for KOH in Solutions of KOH – KCl Mixtures Having a Constant Total Molality of 3.5

m_{KOH}	E	E mean	$\frac{E}{.1183}$	$\log \sqrt{\frac{3.5 \times m_{KOH(s)}}{0.108}}$	$\log \sqrt{\frac{\gamma_{K(s)}\ \gamma_{OH(s)}}{a_{HO_2(s)}}}$	$\sqrt{\frac{\gamma_{K(s)}\ \gamma_{OH(s)}}{a_{H_2O(s)}}}$	γ [$\gamma a108 = .776$]	$\log \gamma$
3.5	.20412 .20423	.20418	1.7257	1.5106	.2151	1.641	1.2734	.10995
3.0	.19511 .19487	.19499	1.6484	1.9772	.1712	1.483	1.1508	.06104
2.5	.18597 .18627	.18609	1.5732	1.4375	.1357	1.367	1.0608	.02563
2.0	.17654 .17618	.17636	1.4908	1.3891	.1017	1.264	.9809	.00838
1.5	.1648 .1639	.1644	1.3894	1.3267	.0627	1.155	.8963	.04755
1.0	.14970 .14976	.14973	1.2656	1.2386	.0270	1.064	.8257	.08318
.5	.1280 .1284	.1282	1.0835	1.0871	−.0036	.9918	.7696	−.11373

TABLE II

Series B

Activity Coefficient Data for NaOH in Solution of NaOH — NaCl Mixtures Having a Constant Total Molality of 5.0

m_{NaOH}	E	E mean	$\frac{E}{.1183}$	$\log \frac{\sqrt{5 \times m_{NaOH(s)}}}{0.108}$	$\log \sqrt{\frac{\gamma_{NA(s)}\ \gamma_{OH(s)}}{a_{H_2O(s)}}}$	$\sqrt{\frac{\gamma_{NO(s)}\ \gamma_{OH(s)}}{a_{H_2O(s)}}}$	$\gamma\ [\gamma .108 = .757]$	$\log \gamma$
.5	.13968 .13839 .13741	.13849	1.1706	1.1655	.0051	1.012	.7661	−.1157
1.0	.15871 .15837	.15854	1.3401	1.3161	.0240	1.0569	.7999	−.0969
1.5	.17034 .16967	.17000	1.4370	1.4041	.0329	1.0787	.8166	0.08799
2.0	.17953 .17944	.17949	1.5172	1.4665	.0507	1.1236	.85056	.07029
2.5	.18757 .18754	.18756	1.5849	1.5150	.0699	1.1750	.8895	−.05085
3.0	.19137 .19425	.19425	1.6920	1.5546	.0874	1.2229	.9257	−.63353
3.5	.20028 .19455	.20028	1.6929	1.5881	.1048	1.2729	.9636	−.0161
4.0	.20696 .20725	.20710	1.7506	1.6171	.1335	1.3598	1.0294	.01259
4.5	.21372 .21438	.21372	1.8065	1.6427	.1638	1.458	1.1039	.04293
5.0	.21851 .21821	.21836	1.8449	1.6655	.1794	1.5115	1.1442	.05849

TABLE III

SERIES C

ACTIVITY COEFFICIENT DATA FOR NaOH IN SOLUTIONS OF NaOH NaCl MIXTURES HAVING A CONSTANT TOTAL MOLALITY OF 3.

m_{NaOH}	E	$\frac{E}{mean}$	$\frac{E}{.1183}$	$\log \frac{\sqrt{3 \times m_{NaOH(s)}}}{.106}$	$\log \sqrt{\frac{\gamma_{Na(s)}\ \gamma_{OH(s)}}{a_{H_2O(s)}}}$	$\sqrt{\frac{\gamma_{Na(s)}\ \gamma_{OH(s)}}{a_{H_2O(s)}}}$	γ [γ106 = .758]	log γ
.5	.11915 .11901	.11908	1.0066	1.06274	−.05614	.8787	.6660	−.17653
1.0	.13853 .13831	.13842	1.1704	1.21323	−.04283	.9061	.6868	−.16317
1.5	.15037 .15032	.15034	1.2711	1.30129	−.03019	.9328	.7071	−.15052
2.0	.15975 .15954	.15965	1.3495	1.36377	−.01427	.9677	.7335	−.1346
2.5	.16728 .16751	.16740	1.4150	1.41198	.0030	1.007	.7633	−.1173
3.0	.17433 .17434	.17434	1.4765	1.45191	.0246	1.058	.8019	−.0959

Discussion of Results

The curve obtained by plotting value of log γ_{KOH} against concentration of KOH appears to be a straight line. Therefore, the law of the linear variation of the log γ with the concentration holds for potassium hydroxide potassium chloride mixtures of constant total molality up to 3.5M. That is the equation

$$\log \gamma = \alpha c + \log \gamma_o$$

holds for solutions nearly saturated with potassium chloride.

The slope of this line gives the value of the constant α and the y intercept gives the value of log γ_o. Using the values obtained from the curve the equation becomes

$$\log \gamma = .0720c - .152$$

Table IV gives the observed values of γ, the values of γ calculated from the above equation and Δ the difference between the observed and calculated values. In the fourth column Δ is given in millivolts.

Both plots of values of γNaOH against the concentration of the sodium hydroxide had a decided curvature showing that in the case of the sodium chloride–sodium hydroxide mixtures there is a decided departure from the law. This departure was calculated as follows:

Straight lines are drawn through the points on the curves corresponding to .5M, 1.M. and 1.5 M. The slopes of these lines are taken as the values of α and the y intercepts as the values of log γ_o.

Thus for the curve representing the series of 5 M total molality the equation becomes

$$\log \gamma = .0284c - .1306$$

And for the curve representing the series of 3 M. total molality the equation is,

$$\log \gamma = .0266c - .1898$$

Table V gives observed and calculated values of γ for the 5 molal series and table VI the observed and calculated values for

the 3 molal series, Δ representing as before the difference between the observed and calculated values.

TABLE IV

Series A

Observed and Calculated Activity Coefficients of KOH in Solution in KOH–KCl Mixtures

c_{KOH}	γ [obs.]	γ [calc.]	Δ	Δ millivolts
0.5	.7696	.7656	.0040	.266
1.0	.8257	.8317	−.0060	.368
1.5	.8963	.9028	−.0065	.368
2.0	.9809	.9817	−.0008	.041
2.5	1.0608	1.0660	−.0052	.249
3.0	1.1508	1.1590	−.0082	.358
3.5	1.2734	1.2590	.0144	.583

TABLE V

Series B

Observed and Calculated Activity Coefficients of NaOH in Solution in NaOH–NaCl Mixtures

c_{NaOH}	γ [obs.]	γ [calc.]	Δ	Δ millivolts
0.5	.7661	.7666	−.0005	.033
1.0	.7999	.7903	.0096	.617
1.5	.8166	.8166	.0000	.000
2.0	.8506	.8437	.0069	.418
2.5	.8895	.8717	.0178	1.04
3.0	.9257	.9007	.0250	1.42
3.5	.9636	.9307	.0329	1.81
4.0	1.0294	.9616	.0678	3.59
4.5	1.1039	.9935	.1104	5.66
5.0	1.1442	1.0260	.1182	5.85

TABLE VI

SERIES C

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS OF NaOH IN SOLUTION IN NaOH–NaCl MIXTURES

c_{NaOH}	γ [obs.]	γ [calc.]	Δ	Δ millivolts
0.5	.6600	.6660	−.0060	.464
1.0	.6868	.6868	.0000	.000
1.5	.7071	.7081	−.0010	.073
2.0	.7335	.7301	.0034	.233
2.5	.7633	.7528	.0105	.710
3.0	.8019	.7762	.0257	1.69

SUMMARY AND CONCLUSION

Measurements were made of the activity coefficients of potassium hydroxide in aqueous solutions of potassium hydroxide-potassium chloride mixtures having constant total molality. The law of the linear variation of the logarithm of the activity coefficient with the concentration holds for this case.

Two series of measurements were made of the activity coefficients of sodium hydroxide in aqueous solutions of sodium hydroxide-sodium chloride mixtures. For the first series the total molality was kept at 5 and for the second series at 3. In neither series did the activity coefficient obey the law of the linear variation of log γ with the concentration. The Deviations from the law were calculated.

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